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"Process to make nano-structurated emitters for incandescence light sources"

The present invention relates to a process to make a nano-structured emitter element for light sources, which can be led to incandescence through the passage of electric current.

Metal components having nanometric surface structures or reliefs, arranged according to specific shapes or geometries, are currently used in some technological fields, such as micro electro-mechanical systems or MEMS, so as to obtain diffractive optical arrangements, medical devices, microturbines, and so on.

The present invention is based on the acknowledgement that nano-structured filaments can find important applications in the field of incandescence lamps. In said light, the present invention aims at suggesting a new process to make in a simple and economical way filaments or similar emitters for incandescence light sources, having nanometric reliefs or structures.

Said aim is achieved according to the present invention by a process to make an emitter as referred to above, characterized in that it envisages the use of a layer made of anodized porous alumina as sacrificial element for the selective structuring of the emitter.

The use of the aforesaid alumina layer enables to obtain a plurality of reliefs on at least a surface of the emitter, or a plurality of cavities within the emitter. Said nanometric reliefs or cavities are arranged on the emitter according to a predefined geometry.

Preferred characteristics of the process according to the invention are referred to in the appended claims, which are an integral part of the present description.

Further aims, characteristics and advantages of the present invention will be evident from the following detailed description and from the accompanying drawings, provided as a mere illustrative, non-limiting example, in which:

- Figure 1 is a schematic perspective view of a portion of a porous alumina film;

- Figures 2-5 are schematic views showing some steps of a film-building process for an alumina film as the one shown in Figure 1;

- Figure 6 is a schematic perspective view of a portion of a first nano-structured emitter as can be made according to the invention;

- Figure 7 is a schematic perspective view of a portion of a second nano-structured emitter as can be made according to the invention;

- Figures 8, 9 and 10 are schematic sections showing three different possible implementations of the process according to the invention, as can be used to make a nano-structured emitter as shown in Figure 6;

- Figures 11, 12 and 13 are schematic sections showing three different possible implementations of the process according to the invention, as can be used to make a nano-structured emitter as shown in Figure 7;

- Figure 14 shows schematic sections of a further possible implementation of the process according to the invention, as can be used to make a nano-structured emitter as shown in Figure 6;

- Figure 15 shows schematic sections of a further possible implementation of the process according to the invention, as can be used to make a nano-structured emitter as shown in Figure 7;

- Figure 16 shows schematic sections of a further possible implementation of the process according to the invention, as can be used to make a nano-structured

emitter as shown in Figure 6;

- Figure 17 shows schematic sections of a further possible implementation of the process according to the invention, as can be used to make a nano-structured emitter as shown in Figure 7.

In all its possible implementations, the process according to the present invention envisages the use of a highly regular film made of anodized porous alumina as sacrificial element or template; depending on the case, said alumina layer is used directly to obtain the desired nano-structured emitter, or indirectly to make a further sacrificial element required to obtain the aforesaid emitter.

Porous alumina films have attracted attention in the past for applications such as dielectric films in aluminum capacitors, films for the retention of organic coatings and for the protection of aluminum substrates.

The structure of porous alumina can be ideally schematized as a network of hollow columns immersed in an alumina matrix. Porous alumina can be obtained by anodization of highly pure aluminum sheets or of aluminum films on substrates like glass, quartz, silicon, tungsten, and so on.

Figure 1 shows by mere way of example a portion of a porous alumina film, globally referred to with number 1, obtained by anodic oxidation of an aluminum film on a convenient substrate, the latter being referred to with number 2. As can be seen, the alumina layer 1 comprises a series of basically hexagonal cells 3 directly close to one another, each having a straight central hole forming a pore 4, basically perpendicular to the surface of the substrate 2. The end of each cell 3 placed on the substrate 2 has a closing portion with basically hemispheric shape, all closing portions building together a non-porous part of the film 1, or

barrier layer, referred to with number 5.

As is known from the prior art, the film 1 can be developed with a controlled morphology by suitably selecting the electrolyte and process physical and electrochemical parameters: in acid electrolytes (such as phosphoric acid, oxalic acid and sulfuric acid) and under suitable process conditions (voltage, current, stirring and temperature), highly regular porous films can be obtained. To said purpose the size and density of cells 3, the diameter of pores 4 and the height of film 1 can be varied; for instance the diameter of pores 4, which is typically of 50-500 nm, can be increased or decreased through chemical treatments.

As schematically shown in Figure 2, the first step when making a porous alumina film 1 is the deposition of an aluminum layer 6 onto the substrate 2, the latter being for instance made of silicon or tungsten. Said operation requires a deposit of highly pure materials with thicknesses of one micron to 30 microns. Preferred deposition techniques for the layer 3 are thermal evaporation via e-beam and sputtering.

The step including the deposition of the aluminum layer 6 is followed by a step in which said layer is anodized. The anodization process of the layer 6 can be carried out by using different electrolytic solutions depending on the desired size and distance of pores 4.

Should the electrolyte be the same, concentration, current density and temperature are the parameters that greater affect the size of pores 4. The configuration of the electrolytic cell is also important in order to obtain a correct distribution of the shape lines of the electric field with a corresponding uniformity of the anodic process.

Figure 3 schematically shows the result of the first anodization of the aluminum layer 6 onto the sub-

strate 2; as schematically pointed out, the alumina film 1A obtained through the first anodization of the layer 6 does not enable to obtain a regular structure. In order to obtain a highly regular structure, such as the one referred to with number 1 in Figure 1, it is thus necessary to carry out consecutive anodization processes, and in particular at least

i) a first anodization process, whose result can be seen in Figure 3;

ii) a reduction step through etching of the irregular alumina film 6, carried out by means of acid solutions (for instance CrO_3 and H_3PO_4); Figure 4 schematically shows the substrate 2 after said etching step;

iii) a second anodization of the part of alumina film 1A that has not been removed through etching.

The etching step referred to in ii) is important so as to define on the residual alumina part 1A preferential areas for alumina growth in the second anodization step.

By performing several times the consecutive operations involving etching and anodization, the structure improves until it becomes uniform, as schematically shown in Figure 5, where the alumina film referred to with number 1 is now regular.

As shall be seen below, in some implementations of the process according to the invention, after obtaining the regular porous alumina film 1, a step involving a total or local removal of the barrier layer 5 is carried out. The barrier layer 5 insulates the alumina structure and protects the underlying substrate 2: the reduction of said layer 5 is therefore fundamental so as to perform, if necessary, consecutive electrodeposition processes requiring an electric contact, and etching processes, in case three-dimensional nano-

structures should be obtained directly on the substrate 2.

The aforesaid process involving the removal or reduction of the barrier layer 5 can include two consecutive stages:

- widening of pores 4, performed in the same electrolyte as in previous anodization, without passage of current;

- reduction of the barrier layer 5, performed by passage of very low current in the same electrolyte as in previous anodization; at this stage the typical balance of anodization is not achieved, thus favoring etching process with respect to alumina-building process.

As mentioned above, according to the invention the alumina film 1 generated through the process previously described is used as template for nano-structuring, i.e. as a base to make structures reproducing the same pattern of alumina. As shall be seen, depending on the selected implementation, it is thus possible to make negative nano-structures, i.e. basically complementary to alumina and therefore having columns on the pores of the film 1, or positive nano-structures, i.e. basically identical to alumina and therefore with cavities on the pores 4 of the film 1.

Figures 6 and 7 show in a partial and schematic way two filaments for incandescence light sources having the two types of structures referred to above, which can be carried out according to the invention; the filament referred to with number 10 in Figure 6 has the aforesaid negative structure, characterized by a base portion 11 from which the aforesaid columns referred to with number 12 start; the filament referred to with number 13 in Figure 7 has the aforesaid positive structure, characterized by a body 14 in which the

aforesaid cavities referred to with 15 are defined.

The techniques suggested to make structured filaments 10, 13 as in Figures 6 and 7 can be quite different, and can include in particular additional techniques (such as evaporation, sputtering, Chemical Vapor Deposition, screen printing and electrodeposition), subtractive techniques (etching) and intermediate techniques (anodization of metal underlying alumina).

To this purpose some possible implementations of the process according to the invention are now described in the following.

First implementation

Figure 8 schematically shows some steps of a first implementation of the process according to the invention, so as to make negative structures as the one of filament 10 in Figure 6.

The first four steps of the process include at least a first and a second anodization of a corresponding aluminum layer on a suitable substrate, as previously described with reference to Figures 2-5; the substrate 2 can be for instance made of silicon and the aluminum layer for the anodization processes can be deposited by sputtering or e-beam.

After obtaining the film 1 having a regular alumina structure (as can be seen in Figure 5), the material to be nano-structured is deposited as a film onto alumina through sputtering; thus, as shown by way of example in part a) of Figure 8, the pores of alumina 1 are filled with the deposited material, tungsten for instance, referred to with number 20.

This is followed by the removal of alumina 1 and of its substrate 2 through etching, as shown in part b) of Figure 8, thus obtaining the desired filament 10 with negative nano-structure, here made of tungsten.

Sputtering technique consists in depositing films

of highly pure material 20 with a thickness of 1 to 30 micron, but does not enable to reproduce structures having a high aspect ratio in an ideal way; the implementation described above is therefore used when the diameter of alumina pores 4 is at its maximum.

Therefore, instead of sputtering, the deposition of material 20 can be performed through Chemical Vapor Deposition or CVD, which is regarded as the most suitable technique for making structures of highly pure or conveniently doped metal. The main feature of this technique is the use of a reaction chamber containing reducing gases, which enable metal penetration into the hollow pores of alumina and the deposit of a continuous layer onto the surface. This ensures a faithful reproduction of high aspect ratio structures.

Second implementation

As for the previous case, this implementation consists in making negative structures, as the one of filament 10 in Figure 6; the implementation basically includes the same initial steps as those of the first implementation, as far as the deposition of the aluminum layer 6 onto the substrate 2 (Figure 2), a first anodization (Figure 3) and a subsequent etching (Figure 4) are concerned. The second anodization (Figure 5) is here performed in order to make a film 1 of thicker porous alumina than in the first implementation.

The thick alumina film 1 is then taken off its support 2 and opened at its base, so as to remove the barrier layer previously referred to with number 5, in a known way. The resulting structure of film 1 without its barrier layer can be seen in part a) of Figure 9.

The following step, as in part b) of Figure 9, consists in the thermal deposition, or deposition through sputtering, of a conductive metal film 21 onto alumina 1. A tungsten alloy 22 is then electrodeposited

onto the structure thus obtained, as in part c) of Figure 9, which alloy fills the pores of alumina 1. Then alumina 1 and its metal film 21 thereto associated are then removed, thus obtaining the desired nano-structured filament 10 made of tungsten alloy, as can be seen in part d) of Figure 9.

Third implementation

This implementation consists in making negative structures as the one of filament 10 in Figure 6, with the same initial steps as those in previous implementations (Figures 2-5).

As shown in part a) of Figure 10, the second anodization is here followed by a step in which a serigraphic paste 23 is deposited onto porous alumina 1, so as to fill its pores.

This is followed by a step in which said paste 23 is sintered, as in part b) of Figure 10, and then alumina 1 and its substrate 2 are removed, so as to obtain the structure 10 as in part c) of Figure 10.

This implementation enables to exploit low-cost technologies and ensures flexibility in the choice of materials. The preparation of the serigraphic paste is the first step of the process; the correct choice of the metal nano-powder, for instance comprising tungsten, solvent and binder, is fundamental to obtain a paste having ideal granulometric and rheologic properties for different types of substrates 2.

Fourth implementation

This implementation of the process according to the invention aims at making positive structures as the one of filament 13 of Figure 7, starting from a template obtained according to previous implementations.

Basically, therefore, one of previous implementations is first used to obtain a substrate having the same structure as the one of filaments previously re-

ferred to with number 10; onto said substrate, referred to with number 10A in part a) of Figure 11, is then deposited a layer of the material 24 required to obtain the final component, for instance tungsten, through sputtering or CVD, as shown in part b) of Figure 11; the material 24 thus covers the columns 12A of the aforesaid substrates 10A, which acts as a template.

Then the substrate 10A is taken off through selective etching, so as to obtain the filament 13 with positive nano-porous structure, as can be seen in part d) of Figure 11, provided with corresponding cavities 15.

The substrate 10A, obtained according to the first three implementations described above, is not necessarily made of tungsten. In a possible variant, onto the substrate 10A, obtained as in Figures 8-9, a metal serigraphic paste 25 is deposited, as in parts a) and b) of Figure 12, which is then sintered, as in part c) of Figure 12. The substrate 10A is then taken off through selective etching, so as to obtain the filament 13 with positive nano-porous structure, as can be seen in part d) of Figure 12.

<u>Fifth implementation</u>

Also this implementation of the process according to the invention aims at carrying out positive nano-structures as the one of the filament previously referred to with number 13, and includes the same initial steps as those shown in Figures 2-5, with the deposition of an aluminum layer 6 through sputtering or e-beam onto a tungsten substrate 2 (Figure 2), followed by a first anodization of aluminum 6 (Figure 3) and an etching step (Figure 4), so as to provide the substrate 2 with preferential areas for the growth of alumina 1 during the second anodization (Figure 5).

The barrier layer 5 of alumina 1 is then removed,

thus opening the pores 4, as can be seen in part a) of Figure 13. This is followed by a step of *Reactive Ion Etching* (RIE), which allows to "dig" selectively in the substrate 2 on the open bottom of the pores 4 of alumina 1, as can be seen in part b) of Figure 13.

The residual alumina 1 is eventually removed, so that the tungsten substrate forms a body 14 with regular nanometric cavities 15, thus obtaining the desired filament 13.

The Reactive Ion Etching step can be replaced, if necessary, by a selective wet etching step or by an electrochemical etching step.

<u>Sixth implementation</u>

This implementation of the process aims at making negative structures as the one of filament 10 of Figure 6 and its initial steps are the same as in previous implementation. Therefore, after obtaining a regular film of alumina 1 on the corresponding tungsten substrate 2 (Figure 5), the barrier layer 5 is removed, so as to open the pores 4 on the substrate 2, as can be seen in part a) of Figure 14. This is followed by an electrochemical deposition of a tungsten alloy 26 with pulsed current, as schematically shown in part b) of Figure 14, and eventually by the removal of residual alumina 1 and of its substrate 2, so as to obtain the desired filament 10, as can be seen in part c) of Figure 14.

The process 6 first consists in preparing the concentrated electrolytic solution for tungsten deposition into the pores 4 of alumina 1; the electrolyte is very important for correctly filling the pores, since it ensures a sufficient concentration of ions in solution. The pulsed current step enables to carry out the copy of structures with high aspect ratio, and sequentially includes

i) the deposition of the tungsten alloy 26 by ap-

plying a positive current; this results in a given impoverishment of the solution close to the cathode made of alumina 1 and its substrate 2;

ii) a relax time, without current application, so as to let the solution be re-mixed close to the cathode;

iii) the application of negative current, designed to remove a part of the alloy 26 previously deposited onto the cathode, thus enabling a better leveling of deposited surface.

Steps I), ii) and iii), each lasting for a few milliseconds, are cyclically repeated until the desired structure is obtained.

<u>Seventh implementation</u>

This implementation aims at making positive nanostructures as the one of filament 13 starting from a substrate with negative structure, obtained through previous implementation, though not necessarily made of tungsten; the aforesaid substrate with negative structure acting as template is referred to with number 10A in part a) of Figure 15.

A tungsten layer 27 is deposited onto said substrate 10A through CVD or sputtering, as can be seen in part b) of Figure 15. This is followed by a selective etching step, so as to remove the substrate 10A, thus obtaining the desired filament 13 with tungsten nanoporous structure, as can be seen in part c) of Figure 15.

<u>Eighth implementation</u>

This implementation aims at making negative nanostructures as the one of filament 10 of Figure 6, and its initial steps are the same as those shown in Figures 2-5, with the deposition of an aluminum layer 6 through sputtering or e-beam onto a tungsten substrate 2 (Figure 2), followed by a first anodization of alumi-

num 6 (Figure 3) and an etching step (Figure 4), so as to provide the substrate 2 with preferential areas for the growth of alumina 1 during the second anodization (Figure 5).

This is followed by a step including the anodization of the tungsten substrate 2, so as to induce the localized growth of the latter, which occurs below the pores 4 of alumina 1. Said step, as shown in part a) of Figure 16, basically includes the formation of surface reliefs 2A of the substrate 2, which first cause the barrier layer 5 of alumina 1 to break, and then keep on growing within alumina pores 4.

Through a selective etching with W/W oxide alumina 1 is then removed, so as to obtain the desired filament 10 with negative nano-structure as in part b) of Figure 16.

It should be noted that this implementation is based on a typical feature of some metals, such as tungsten and tantalum, which anodize under the same chemical and electric conditions as aluminum; as mentioned above, said anodization occurs in the lower portion of the pores 4 of alumina 1, thus directly structuring the surface of the substrate 2.

Ninth implementation

This implementation aims at carrying out positive nano-porous structures as the one of filament 13 of Figure 7 starting from a substrate having a negative structure as the one obtained through previous implementation; said substrate acting as template is referred to with number 10A in part a) of Figure 17.

A tungsten alloy 27 is deposited onto said substrate 10A through electrochemical deposition, CVD or sputtering, as shown in part b) of Figure 17. The substrate 10A is then removed through selective etching, thus obtaining the desired filament 13 with positive or

nano-porous structure.

From the above description it can be inferred that in all described implementations the process according to the invention includes the use of an alumina layer 1 which, depending on the case, directly acts as template so as to obtain the desired filament with nanometric structure 10, or which is used to obtain a template 10A for the subsequent structuring of the desired filament 13.

The invention proves particularly advantageous for the structuring of filaments for incandescence light sources, and more generally of components also under a different form with respect to a filament which can be led to incandescence through a passage of electric current. It should be noticed that an emitter made according to the invention can also be formed by plurality of layers structured by means of porous alumina according to the above describes techniques, in the form of superimposed structured layers.

The described process enables for instance to easily define, on one or more surfaces of a filament, for instance made of tungsten, an antireflection microstructure comprising a plurality of microreliefs, so as to maximize electromagnetic emission from filament into visible spectrum. The invention can be advantageously applied also to make other photon crystal structures, i.e. in structures made of tungsten or other suitable materials characterized by the presence of series of regular microcavities, which contain a medium with a refractive index differing from the one of tungsten or other material used.

Obviously, though the basic idea of the invention remains the same, construction details and embodiments can widely vary with respect to what has been described and shown by mere way of example.